the other elements have also been excessive as compared with their average amounts.

Thus, the mean distance of the meteors occupying segment A of the stream has been undergoing so much extension, that the meteors will at the end of the revolution find themselves with a periodic time longer by one-third of a year—an amount of change which must largely affect their future history, unless this great perturbation is compensated by what happens elsewhere or at other times.

At the epoch 1899, November 15, the longitude of the node will be 53° 41′·7, a position which the earth will reach on 1899, November 15d. 18h. It is probable, therefore, that the middle of the shower of the present year (1899) will occur nearly at this time, since segment A in the stream, for which our calculations have been made, is situated in the stream less than three months' journey of the meteors behind the segment which the earth will encounter next November, and which we may call segment B. This conclusion, however, rests on two assumptions: (1) That segments A and B were, in 1866, moving in orbits that did not much differ; (2) That the perturbations which segments A and B have since suffered have not much differed. Both assumptions are probable, but unfortunately neither is certain; so that the prediction can only be offered with reservation. If the shower occurs at the time anticipated, it will be visible from both Europe and America.

"On Hydrogen Peroxide as the active Agent in producing Pictures on a Photographic Plate in the Dark." By W. J. Russell, Ph.D., V.P.R.S. Received February 18,—Read March 2, 1899.

In previous papers it has been shown that certain bodies are able, in the dark, to act on a photographic plate and produce a picture. The purpose of the present communication is to show that in all the cases which have been examined, and probably in all others of a similar kind, the action which occurs is due to the presence of hydrogen peroxide. As a sensitive plate always contains moisture, and probably would be inactive if quite dry, it does not seem possible to test the truth of this statement by the total exclusion of moisture; therefore more indirect means have to be adopted. In the following paper no attempt is made to explain the reactions which occur in the plate itself; that is a distinct question, and at present the object is to consider the means by which these changes, whatever they may be, are brought about. These changes are rendered visible by exactly the same processes as those adopted for the development of an ordinary light picture. Any of the ordinary photographic plates may be used in

these experiments, but as many of the pictures are only formed after a long exposure, it is well to use rapid plates. In the following experiments the plate used has been in almost all cases the "Ilford special rapid," and the process of development has in every case been that recommended for their ordinary use.

The first step towards demonstrating that hydrogen peroxide is the active agent in producing these pictures, is to show that all the results produced both by metals and by organic bodies on a photographic plate, can be produced by hydrogen peroxide. This body is now made in considerable quantities and sold in aqueous solution of a given strength. This commercial article appears to act equally well to a carefully prepared and pure specimen of the same strength.

A convenient way of testing the action of any liquid on a photographic plate is to use a small circular glass dish, such as is made for bacteriological experiments, the photographic plate resting on the top of the dish, and the amount of the liquid used determines the distance the plate is from the active surface, the experiment being carried on in complete darkness. If pure water be tested in this way, it is found that no picture, that is no darkening of the plate, occurs on its being treated with the developing solution. The plate can be left over the water for eighteen to twenty hours, but if left longer than this, the film is destroyed by the aqueous vapour. If to the pure water in the dish a mere trace of hydrogen peroxide be added, a darkening of the plate will quickly occur. For instance, if the liquid contains only one part of the peroxide in a million of water, and the plate be exposed to its action for eighteen hours, a faint picture is produced. Bearing in mind the small amount of evaporation which takes place under these conditions, and consequently the minute amount of the peroxide which comes in contact with the plate, it clearly shows the exceeding delicacy of the reaction.

Again, if a piece of Ford blotting paper, which by itself is inactive, after being wetted with a solution of one part of peroxide in 500,000 of water, and hung up in a warm room for three quarters of an hour to dry, is placed in contact with a photographic plate for two hours at a temperature of 55° C., on subjecting the plate to development a distinct picture is produced. In fact, moistening good blotting-paper with a solution which may be strong or weak, and allowing it to dry for a long or short time, is a very good way of applying the peroxide. In place of blotting paper any inactive porous substance may be used.

Plaster of Paris wetted with a peroxide solution and allowed to set, continues for a long time to be an active body. If by any of these means a large, in place of a small, amount of the peroxide be allowed to act on a plate, then in place of a dark, a light picture is obtained, a phenomenon similar to what is known to photographers as reversal.

The conditions under which certain metals and certain organic bodies

act on photographic plates, and how pictures of the structure of paper, skeleton leaves, lace, and other bodies can be obtained, has already been described, so that now it is only necessary to say that substitute for these active bodies peroxide of hydrogen, and exactly corresponding results are produced. Writing with ordinary ink, or with a solution of ferrous sulphate, or potassium ferrocyanide, has been shown to be opaque to the action of zinc and of turpentine, so is it to the action of the peroxide of hydrogen. Further, the action exerted by the metals and the terpenes, is unable to pass through glass, mica, selenite, &c., but is able to pass through thin sheets of gelatin, celluloid, gutta-percha, india-rubber, tracing paper, gold beaters' skin, parchment, &c. Peroxide of hydrogen acts exactly in the same way; every body which is known to be either opaque or transparent to the action of the metals or terpenes, is opaque or transparent to the action of the peroxide; so that as far as the production of similar phenomena goes, the agreement is complete. Of the acknowledged tests for the presence of hydrogen peroxide, the one with the titanic acid dissolved in sulphuric acid is exceedingly delicate; so also appears to be the tetramethylparaphenylenediamine paper of Dr. Wurster, and both of them have been made use of.

The next point which naturally suggests itself is, whether peroxide of hydrogen is, or is likely to be, present in all the different cases, when action on the sensitive plate occurs. First, with regard to the metals. The list of the active metals, which has already been given, is as follows, arranged approximately in order of their activity: Magnesium, cadmium, zinc, nickel, aluminium, lead, cobalt, bismuth, tin. Now these are certainly the metals which might be expected to decompose water, and in the presence of oxygen cause the formation of hydrogen peroxide; and still more the order in which they stand in the above list, judging from their general properties, is that in which they would probably induce the formation of the peroxide. It is also satisfactory to note that this list of metals and their order of activity was drawn up simply from experiment, when there was no idea that hydrogen peroxide had anything to do with the reaction. Again, as a confirmation that hydrogen peroxide is formed when these metals oxidise in moist air, pieces of Dr. Wurster's tetra-paper were moistened and laid on bright surfaces of the metal. With the metals that head the foregoing list a considerable amount of blue colour was rapidly developed, with the metals at the end of the list the amount of colour was less, and the reaction slower; and with other metals, such as silver and platinum, there was no action. With copper and with iron a very slight amount of action did occur, but these metals do not appear able to produce definite pictures. Iodide of potassium and starch paper, when used in the same way, gave a blue colour with all the active metals, but none with copper nor with iron.

On the supposition that hydrogen peroxide is the active agent in the action exerted by the metals, it seemed probable that on supplying to the metal more moisture than it obtained from the air and photographic plate, more action would take place, and this was found to be the case. Two pieces of polished zinc were placed in contact with photographic plates in small iron boxes; one box was quite dry, and put in a bell-jar over calcium chloride, and into the other box some damp paper was introduced, and the box was placed with a little water under a bell-jar. On examining the plates after three days it was found that the damp plate had much the darker picture on it.

With the object of obtaining an increased amount of action, experiments were made by passing a current of warm moist air over zinc turnings. A glass tube, 6 feet long and 1 inch in diameter, was packed with zinc turnings, and placed within a large brass tube to which steam could be admitted. The amount of action, if any, was indicated on a plate, placed in a dark box at the end of the tube. Even under the most favourable conditions no very large amount of action took place. When a current of moist warm air was passed through the tube for an hour a fairly dark picture was obtained. If the air was dry no picture appeared. If amalgamated zinc was used in place of pure zinc a darker picture was formed, and, as a check on these results, dry and moist air, both warm and at ordinary temperatures, was passed through the tube, no zinc being present, and then no action took place. Also when ozonised air was passed through the tube there was no action. Passing now from the metals to the organic bodies capable of acting on a photographic plate, it has been found that they belong essentially, if not solely, to that class of bodies known as terpenes, and it is a general property of all this class of bodies when oxidising to give rise to hydrogen peroxide. Thanks to Dr. Tilden, experiments have been made with most of the terpenes, and all were found to be very active bodies; both pinene and limonene were tried, in their dextro- and lævo-rotatory state, but their activity appeared to be the same. Oxidised and other compounds connected with the terpenes, such as terpineol camphor, thymol cymene, have no power of acting on a photographic plate, but ordinary turpentine and terebene are very active bodies.

Most of the ordinary essential oils, such as bergamot, peppermint, pine, lemons, cajuput, &c., have been experimented with, and, without exception, have been found to be active bodies. It is well known that they all contain terpenes. They are also characterised by a strong odour, and as ordinary scents contain some of these bodies, it follows that almost all vegetable bodies having a strong smell are capable of acting on a photographic plate. Eau de Cologne gives a good picture, so do many wines and brandy, and coffee, guaiacum, cinnamon are also active substances; thus the photographic plate becomes a very delicate

test for the presence of all these bodies, and as the action is cumulative it may even compete with the sense of smell.

In addition to the essential oils, the ordinary vegetable oils, such as linseed oil, which is the most active, and colza and olive, which are much less active and have much less power of absorbing oxygen from the air, can act on a photographic plate. The tetra-paper readily goes blue if suspended in a bell-jar which has a few drops of linseed oil in a dish within it.

The mineral oils are, on the contrary, devoid of this power of acting on the sensitive plate, and the same applies to bodies such as benzene, phenol, naphthalene, aldehyde, methyl alcohol, coal naphtha, &c.

It would seem, then, that all the organic bodies capable of acting on the photographic plate are capable of giving rise to the formation of hydrogen peroxide when they oxidise in moist air.

In former papers it has been shown that the active bodies, both metallic and organic, are able to act on a photographic plate even when thin layers of many different substances are interposed; for instance, if a thin sheet of gelatin be laid on a polished zinc plate it only very slightly modifies either the sharpness of the picture or the time required for its production. If the gelatin plate be thicker the action will still pass through, but the picture will be more indistinct, and the time necessary for its production longer. If a 2 per cent. solution of hydrogen peroxide be poured into one of the small glass dishes, and a sheet of gelatin 0·0013 inch thick be placed over it $\frac{1}{8}$ inch above the liquid, a picture will be obtained in fifteen minutes. If the sheet of gelatin be 0·008 inch thick, then the exposure must be for one hour; and if the gelatin be 0·01 inch thick, an exposure of three hours is necessary. If a sheet of celluloid be substituted for the gelatin, and it be 0·005 inch thick, the action still passes through, but more slowly than through the gelatin, and the plate now requires one hour exposure to give a good picture. With a plate of celluloid of double the above thickness, the exposure must be four times as long; and if the thickness be 0·033 inch, the time of exposure has to be thirty hours. These determinations show well what happens in these cases, but are only good approximations, not standard results. In addition to gelatin and celluloid, guttapercha tissue, india-rubber, tracing paper, collodion, albumin, gold beater's skin, parchment, &c. also allow the action to take place through them, and the obvious question which presents itself is, If hydrogen peroxide be the body which gives rise to the action, how does it pass through these different bodies? Take the definite case of zinc; if a plate of this metal be rubbed with coarse sand paper and placed in contact with a photographic plate, a clear and sharp picture of the scratches is obtained, and it might have been expected that when the action took place through even a very thin sheet of gelatin the picture of the scratches

would have no longer been visible, or at least only indistinctly so, but experiment shows this is not the case. How then does the peroxide permeate the gelatin? Not by the ordinary process of diffusion, for hydrogen cannot diffuse through it, so that it must be by a process of dissolving, or very feebly combining with the medium, or with a constituent of it, and thus travelling through escape on the other side. That the action is of this nature seems rendered probable by the following experiments, which show, at least to some extent, what takes place.

A 2 per cent. solution of hydrogen peroxide was placed in a dish with a sheet of the thinnest gelatin, about one hundredth of an inch thick; above it and on the gelatin a photographic plate was placed, and allowed to remain there for twenty minutes. No picture was formed. Immediately on removing this first plate from the gelatin, a second one was put in its place, and allowed to remain there also for twenty minutes. This plate gave a faint picture, the third one gave a darker picture, and the fourth one was still darker; but the fifth, sixth, and seventh plates were, as far as could be judged by the eye, of the same degree of darkness. Thus the amount of peroxide given off on the upper surface of the gelatin went on increasing for one hour and twenty minutes, and then the action became uniform. The same kind of action occurs if zinc be used in place of peroxide solution. If a thin sheet of gelatin be laid on a piece of zinc and allowed to remain there for a week, then, on placing above it a sensitive plate, a picture will be produced in about one-third to one-fourth the time which would have been necessary if the previous exposure to the zinc had not taken place. Celluloid was found to act exactly in the same way as the gelatin. The plate, after the first half-hour's exposure, gave no pictures, but a faint one after the second half-hour; and it was not till after the fourth half-hour that the action became constant. A thicker specimen, 0·011 inch thick, was also examined after intervals of two hours, it acted in the same way as the other specimens, but required ten and a half hours before the action became uniform. If drying oil or copal varnish be used in place of the peroxide of hydrogen solution, analogous results are obtained. This action explains how pictures can be obtained from invisible originals. If, for instance, a piece of white cardboard or paper is placed behind a copper stencil and is exposed to the vapour from peroxide of hydrogen solution, drying oil or copal varnish, &c., the exposed part of the paper becomes active, although not visibly affected, and on placing it on a sensitive plate, a picture of these parts is produced. Zinc acts in the same way, but only slowly. A zinc ornament, laid on a piece of Bristol board for eight months, charged the board only so far as to enable it to give a faint picture.

Gelatin can be substituted for the paper in these experiments, and can be charged and made to convey a clear picture to a sensitive plate.

It is then evident that the action arising from zinc and other active bodies can, by an intermediate and inactive substance, be carried away and allowed to expend itself at another time and at another place.

With regard to the transmission of the action through gelatin, the water which it contains is probably the body which enables the peroxide to pass through. It can also be shown that it aids the transmission of the action through other inactive bodies, for instance if Bristol board in its ordinary condition be placed on a polished piece of zinc, the action of the zinc only slowly passes through it, but if the board be damp the transmission takes place much more rapidly. The following comparative experiments illustrate this. Two similar pieces of Bristol board were taken, one was dried and then placed between a piece of perforated zinc and a sensitive plate and put under a bell jar with calcium chloride; the other piece of Bristol board was suspended over water until it was thoroughly damp, and then placed between perforated zinc and a sensitive plate under a bell jar with a little water present. Both experiments were continued for twelve days, when it was found that with the dry board there was no picture produced, but with the damp one there was a good and dark one. If copal varnish be used in place of zinc, similar results are obtained, and if parchment be substituted for Bristol board the results are the same.

These experiments are however not conclusive, for it has been shown that with additional amount of water some of it finds its way to the zinc, and there induces the formation of more peroxide which may account for the darker pictures. Even with the terpenes the additional amount of water may induce the additional formation of peroxide. This objection can however be obviated by cutting off the moisture in the damp medium from the active substance, or by using the aqueous solution of the peroxide as the origin of the action. In order to stop the aqueous vapour from either passing from the damp Bristol board or to it from the peroxide solution, a piece of tracing paper is interposed which allows the action to pass through it, but not any appreciable amount of aqueous vapour. On placing a sheet of tracing paper over a glass dish containing the peroxide solution and above it dry Bristol board with a photographic plate, in one and a half hours just an indication of a picture was produced, but when under the same conditions Bristol board which had been over water for nineteen hours was used, then a dark picture was formed. Again similar experiments were made using a not highly glazed paper in place of the Bristol board, and the results were the same.

In place of tracing paper, celluloid was used and the dry Bristol board gave, under similar conditions, no picture, but the damp one gave a very distinct picture. In order to avoid having so much water present, plaster of Paris set by a little of the peroxide solution was used in place of the aqueous solution, and exactly similar results were obtained,

so there is no doubt that hydrogen peroxide can readily pass through a porous body by the aid of water.

Alcohol acts in the same way as water, for when plaster of Paris wetted with peroxide solution was poured into a couple of similar dishes and allowed to set, and over one a piece of dry and over the other a piece of Bristol board moistened with alcohol were placed, and sensitive plates above them, after fifty minutes only a very faint picture was formed above the dry board, but a dark one over the wetted board.

Celluloid is however nearly as transparent to these actions as gelatin, and water in this case cannot be the transmitting medium, so that the question is whether there be any constituent of the celluloid which may act in a similar way to that of water in the gelatin. From the following experiments it seems that camphor can do so :—

Camphor itself like water is a perfectly non-active body. To obtain a thin non-porous layer of this body is difficult, but it is easy to prove that the emanations from hydrogen peroxide solutions, from zinc, copal, or other active bodies, are readily absorbed by it, and readily pass through it. For instance, if a piece of camphor be placed about quarter of an inch above a 2 per cent. solution of hydrogen peroxide for seventeen hours and be then removed and placed on a sensitive plate for fifteen minutes, it gives a dark picture, and when a similar experiment is made using drying oil in place of the peroxide solution, and the camphor be exposed to its action for three days and then brought in contact with the sensitive plate for one day, a dark picture is produced. This action can however be easily carried still further and proved to pass through even a thick layer of camphor. A piece 0·137 inch thick was placed about $\frac{1}{8}$ inch above a 2 per cent. solution of peroxide in a dish, for sixty-six hours, and a sensitive plate placed on the top of it; on treating this photographic plate with the developing solution it was found that a considerable amount of action had occurred. Thus the camphor which is a principal constituent of celluloid may enable hydrogen peroxide to pass through it.

That guttapercha and pure india-rubber should allow the action to pass through them is remarkable. The substance known as guttapercha tissue has a thickness of about 0·003 inch, and allows the action to pass readily through it; in fact, if even two thicknesses of this tissue be placed over the 2 per cent. solution of the peroxide for seventeen hours, a dark picture is obtained. If the tissue be laid on a polished piece of perforated zinc and a sensitive plate above it, after remaining there for a fortnight a fairly good picture is obtained. If drying oil be used, the action will pass through the guttapercha in three days. With regard to this transmission of the action, although the chemical constitution of guttapercha is not well established, it is said to be a

body related to camphor,* and hence the action passes through it as it does through celluloid, and this is borne out by the fact that if a piece of guttapercha be placed for eighteen hours over the 2 per cent. peroxide solution, and then placed for twenty minutes on a sensitive plate, it evidently has become active, for it then gives a good picture.

The above remarks apply also to india-rubber. The thinnest sheet that has been experimented with is 0·017 inch thick; this allowed the action to pass through it, but was too thick to give a picture, but, like the guttapercha, if placed over the peroxide solution it became active, and produced considerable action on a photographic plate.

With regard to other substances which allow the action to take place through them, the most interesting are true gold beater's skin, and albumen. If Bristol board or paper be carefully painted on one side with white of egg and allowed to dry in the air, it forms a medium through which the peroxide can pass. Collodion also allows the action readily to pass through it. In all these cases the tetra-paper may be used to confirm the results obtained.

Then with regard to bodies which do not allow the action to pass through them. Paraffin is one of them. If paper be painted with melted paraffin and it be placed over a solution of the peroxide, no action passes through, neither is it able to absorb the peroxide like camphor and india-rubber and guttapercha. A piece of paraffin placed over the peroxide solution for twenty hours and then tested by placing it on a sensitive plate produced no action.

Gum arabic is a body which sometimes is very opaque, but this is simply a question of hydration, and is confirmatory of what has been said before with regard to the action of water. Some unglazed paper was painted on one side with two coats of good gum arabic, and some of it was dried at 55° for some days, and another portion of it was *air*-dried only for some hours, and both were put over drying oil for three days. The dried paper gave only a very faint picture, but the more moist one a very dark picture.

When experimenting some time ago on the general nature of these reactions, polished zinc was placed below some inactive liquids to test whether any action took place through them. The small glass dishes were used, and a disc of bright zinc laid inside, and the liquid to be tested poured upon it; then the photographic plate was placed on the top of the dish. After remaining there for three or four days the plate was generally found acted on as if the zinc had been able to exert its influence upon it. Lately these experiments have been repeated and extended, and, as indicating the extreme delicacy of the reaction with the photographic plates, are of interest. The form of experiment was the same as described above, and the liquids used were alcohol, ether, ethyl acetate, chloroform, benzene, petroleum spirit. All these liquids

* Bernthsen, 'Organic Chemistry,' p. 509.

were purified, so that when placed in the dish with the sensitive plate above them no action after a week's exposure took place. However, when a zinc disc was introduced below the inactive liquids the photographic plate was generally acted on, but with the benzene and petroleum spirit sometimes no action occurred. These rather singular results were next tested in another way. Portions of these inactive liquids were put into stoppered bottles with polished strips of zinc foil, and allowed to remain there for a week, and it was then found that the liquid had become active, for on testing it by putting it into a dish with a photographic plate above it, a dark picture was formed, so that the action of the zinc was to make the whole of the liquid active. Magnesium, cadmium, aluminium, fusible metal, and bismuth, all produced effects similar to those obtained with the zinc, but nickel, lead, tin, &c., produced no such effects. Further it was proved that a very small amount of peroxide rendered alcohol, for instance, very active; 0·1 c.c. of a 2 per cent. solution of the peroxide added to 10 c.c. of alcohol gave it the power of acting on a sensitive plate $\frac{1}{8}$ inch above its surface, so as to produce in a few hours a dark picture. The still more careful purification of these liquids, and especially the exclusion of moisture, was undertaken, and in every case it was found when all moisture was excluded that the zinc had no longer the power, when below a liquid, of acting on a photographic plate. Specimens of alcohol, ether, and chloroform were prepared, and these when placed in a dish with zinc at the bottom of it (standing over sulphuric acid) allowed no action to pass through them, and when treated for a week or more with bright zinc in a bottle still retained their perfect inactivity. To a sample of the alcohol which in a dish with zinc allowed no action on the sensitive plate above to occur, a trace of water was added, as much as adhered to the end of a thin glass rod, and now with the same length of exposure a dark picture was formed. From these experiments, as well as those previously mentioned, it appears that this action on the photographic plate is one of extreme delicacy.

The action of water alone on zinc is interesting, and appears to confirm the view that hydrogen peroxide is the active agent in all these reactions. It has already been shown that although bright zinc is active, dull zinc is inactive. However, if a piece of bright zinc be placed in water and remains there for twenty-four hours or so, it, of course, oxidises, white spots or lines appear, and, in fact, in time the whole surface would become covered with oxide. Now the oxide thus formed is strongly active. Take the plate out of the water, let it dry, place it in contact with a photographic plate, and a strong picture of the spots of oxide is obtained. No doubt peroxide of hydrogen is formed, and remains entangled in this porous oxide; in fact it is difficult entirely to remove it. The plate, with this oxide on it, may be dried at ordinary temperatures and exposed to the air for a day or two, and

the oxide is still active, or it may be dried over calcium chloride or even exposed to a vacuum for some time, and it is still active, but if heated to 55° for seventeen hours then its activity is gone and a picture the reverse of the former one is obtained, that is, the oxide is now quite inactive, but the metal itself is very slightly active. Oxides of zinc, cadmium, and magnesium, if wetted with peroxide of hydrogen solution, act in the same way and retain their activity with great pertinacity.

From the foregoing experiments it is then concluded that hydrogen peroxide is the agent which directly or indirectly causes the changes in the photographic plate.

This investigation has been carried on in the Davy-Faraday laboratory, and I would again tender my best thanks to the managers of the Royal Institution for allowing me to work there. My thanks are also due to Mr. O. F. Block who has most efficiently helped in carrying on the above experiments.

March 9, 1899.

The LORD LISTER, F.R.C.S., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read:—

I. "A Preliminary Note upon certain Organisms isolated from Cancer, and their Pathogenic Effects upon Animals." By H. G. PLIMMER. Communicated by Dr. ROSE BRADFORD, F.R.S.

II. "On the Gastric Gland of Mollusca and Decapod Crustacea; its Structure and Functions." By Dr. C. A. MACMUNN. Communicated by Professor M. FOSTER, Sec. R.S.

III. "On the Structure and Affinities of *Matonia pectinata*, R. Br., with Notes on the Geological History of the Matonineæ." By A. C. SEWARD, F.R.S.

IV. "A Sugar Bacterium." By Professor MARSHALL WARD, F.R.S., and Professor REYNOLDS GREEN, F.R.S.

V. "Note on a new Form of Light Plane Mirrors." By A. MALLOCK. Communicated by LORD RAYLEIGH, F.R.S.